

# PATENT SPECIFICATION

DRAWINGS ATTACHED

871.750



Date of Application and filing Complete Specification: March 13, 1959.

No. 8759/59.

Application made in United States of America on March 18, 1958.

Complete Specification Published: June 28, 1961.

Index at acceptance:—Classes 1(2), A1C1; and 1(1), L3.

International Classification:—C01b. B01d.

## COMPLETE SPECIFICATION

### Method of Separating Carbon Dioxide from Sulfur Compounds

We, CHEMICAL CONSTRUCTION CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, of 525 West 43rd Street, New York 5, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for the separation of hydrogen sulfide, carbon oxysulfide and/or mercaptans from gases containing carbon dioxide. More particularly, the invention relates to the almost complete elimination of the above specified sulfur-containing compounds from CO<sub>2</sub>, or as may be termed the super-purification of CO<sub>2</sub>.

The invention is of general application in the separation of gas mixtures containing CO<sub>2</sub> and H<sub>2</sub>S, but is of particular importance in purification of CO<sub>2</sub> which is to be used in the synthesis of urea. Since the carbon dioxide used for production of urea is generally derived from starting materials like hydrocarbons or any by-product gases like blast furnace gas, the thus produced gas generally contains up to about 400 p.p.m. of H<sub>2</sub>S or above. Consequently, this gas must be purified to the extent that the H<sub>2</sub>S content is lowered to preferably 2 p.p.m. or less prior to being delivered to a urea synthesis reactor.

It is known that corrosion of the urea reactor equipment is due to the presence of small amounts of hydrogen sulfide in the starting materials. It is further known that the useful life of linings of urea synthesis reactors is lengthened considerably if hydrogen sulfide, carbon oxysulfide and organically bound sulfur, particularly mercaptans, are removed prior to the synthesis reaction. Carbon oxysulfide and mercaptans in themselves do not harm reactor linings such as silver, lead or copper alloys, but under conditions of high pressure and temperature of the urea synthesis reaction these sulfur compounds are decomposed to form the

hydrogen sulfide which is harmful to such materials of construction.

In prior methods of separating H<sub>2</sub>S and organically bound sulfur compounds from CO<sub>2</sub>, it has been the practice to pass the gas mixture through beds of iron oxide or activated charcoal. Various scrubbing solutions of such compounds as sodium carbonate can also be used but CO<sub>2</sub> is also picked up in large amounts in the scrubbing solution and hence H<sub>2</sub>S cannot be completely separated from CO<sub>2</sub> by these processes. The prior method of removing H<sub>2</sub>S most widely accepted has been the iron oxide methyl wherein the H<sub>2</sub>S-containing gas is forced through beds of the adsorbing material to form compounds of iron sulfide by reaction of the H<sub>2</sub>S in the gas with the iron oxide. However, the iron oxide tends to cake and cause excessive back pressure and in general practice the fouled iron oxide is incapable of regeneration. In practice the fouled iron oxide is removed from the beds to be dumped without any attempt at regeneration because in the presence of acidic gases, as CO<sub>2</sub>, regeneration is not possible. Since these prior processes in themselves do not adequately decrease the H<sub>2</sub>S content to the parts per million required by the urea synthesis process, some further scrubbing of effluent gases by solutions of such agents as potassium permanganate is necessary.

In contrast to the prior practice of using iron oxide or other adsorbents as listed above, it has now been found that a high degree of purity can be attained in preparing a CO<sub>2</sub> product for use for example in synthesis of urea by passing said CO<sub>2</sub> gas containing H<sub>2</sub>S through adsorbent beds of dehydrated zeolites which have the surprising property of preferentially and completely removing H<sub>2</sub>S from CO<sub>2</sub> down to about 1 p.p.m. It is to be understood that, when reference is made in this specification to the separation of H<sub>2</sub>S from CO<sub>2</sub>, the reference also applies to the separation of carbon oxysulfide and/or mercaptans from CO<sub>2</sub>. It has been found that these zeolites when

[Pr]

Price 25c

dehydrated make an extremely good separation of  $\text{CO}_2$  and  $\text{H}_2\text{S}$  and can be repeatedly regenerated for extended periods of time without having to be replaced by fresh adsorbent material. This property of the dehydrated zeolites is in marked contrast to the prior types of adsorbent agents used for separation of  $\text{H}_2\text{S}$  from  $\text{CO}_2$  that are not capable of being regenerated and have to be used in conjunction with scrubbing solutions for final cleaning.

We are aware of Patent Specification 777,233 which claims, *inter alia*, a method of using a specific crystalline synthetic zeolitic material for separating mixtures of gases in which, in one embodiment, the crystalline synthetic material is contacted with a mixture of hydrogen sulfide and one or more of the following gases: hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide, methane, ethylene, propane, butane or pentane, and at least a portion of the hydrogen sulphide is adsorbed by the crystalline synthetic material.

The absorbent material used in the operation of this invention is a zeolite having a particular crystalline structure as defined below, said zeolite having been activated by heating to drive off the water of crystallization. This zeolite can be either the naturally occurring mineral or, alternately, a synthetic material having the same physical properties as the natural mineral. Generally, these zeolites are of a structure similar to that present in chabazite. The essential characteristic of this type of dehydrated zeolite which makes it suitable for the process of this invention is that the diameter of the narrowest interstitial channel therein is 4.0 Angstrom units or greater. The mineral within the class of zeolites having these interstitial openings in the crystal structure are: chabazite-like minerals and their synthetic equivalents. The preferred dehydrated zeolites are those whose voids have a narrowest dimension of about 5 Angstrom units. All of these minerals, either in their natural state or as synthesized, contain water of crystallization which must be removed to prepare the material with optimum of physical characteristics for adsorption operation. When the minerals are heated to temperatures of about 350° C., either at atmospheric pressure or under a vacuum, the water of crystallization is driven off, leaving a crystal structure having interstitial voids of the necessary dimensions.

It is well recognized that the natural zeolites and some artificial zeolites can be dehydrated without destroying the crystalline characteristics of the zeolite. This is not true of some of the other zeolites which have a fibrous structure derived from the crystalline habit of the mineral, wherein channels within the dehydrated crystal are less than 4 A. Usually these fibrous zeolites lose their crystalline structure on dehydration, thereby becoming amorphous.

In the preparation of the synthetic zeolite of

the chabazite crystal habit by known methods, the sodium ions in the compound may be replaced either partially or completely by calcium and/or barium.

In accordance with this invention, there is provided a method of separating gases containing carbon dioxide from at least one of the sulfur containing compounds hydrogen sulfide, carbon oxysulfide or mercaptans which comprises passing the dried or undried gases containing  $\text{CO}_2$  and at least one of said sulfur containing compounds through a zeolitic material to preferentially adsorb said sulfur containing compound or compounds, said zeolitic material having been previously activated by heating to drive off the water of crystallization to establish a crystalline structure having interstitial voids whose narrowest dimension is 4.0 Angstrom units or greater, continuing adsorption until the sulfur containing compound break-through reaches from 1 to 2 ppm., discontinuing absorption, regenerating the adsorbent bed by passing a heated regenerating gas through the adsorbent in a manner countercurrent to the flow of gases during adsorption, preparing said adsorbent bed for further adsorption by passing a sulfur-free cooling gas through said bed, countercurrent to the direction of flow of gases during adsorption and recovering separately the purified carbon dioxide and the said sulfur containing compound or compounds.

The apparatus generally comprises a series of vessels of known type containing beds of the dehydrated zeolite through which the impure gas is passed for adsorption of impurities, followed by regeneration and cooling. The invention could be practiced in one or more vessels but the preferred number is three arranged in a manner in accordance with the drawing. Following the accompanying flow diagram for purposes of illustration, the gas to be treated, which is preferably under a pressure of 200 to 500 psig, after passing through a primary drier then passes through the adsorbent bed in vessel 1, while at the same time a previously contaminated bed in vessel 2 is being regenerated by means of a heated gas as hereinafter more fully described. Simultaneously, a hot regenerated bed in vessel 3 is being cooled preparatory to adsorption of additional amounts of impure  $\text{CO}_2$  gas as herein-after more fully described. The impure gas mixture is delivered to the vessels through a pipe 4 and thence into the adsorbent vessel 1. A series of valves 5, 6 and 7, which are located between the pipeline 4 and the adsorbent vessels direct the flow of the gas mixture. Two of the valves remain closed while the adsorption process is carried out in the remaining vessel. Adsorption is allowed to continue in vessel 1 until the hydrogen sulfide content in the gas leaving the vessel rises to 2 p.p.m. of  $\text{H}_2\text{S}$ .

It is preferred that the gas-mixture coming

70

75

80

85

90

95

100

105

110

115

120

125

130

into the adsorber 1 be predried by passage through the drier 9 of known type which may contain such materials as activated alumina or silica gel. A benefit arising from predrying 5 is the increase in the efficiency of the zeolitic adsorbent. However, if the gas mixture is at ambient temperature and superatmospheric pressure, the drier may be eliminated and the gases sent directly to the adsorber 1.

10 At the same time vessel 2, which was previously loaded with  $H_2S$ , is regenerated by heated gases introduced into the system through the line 10. At this time the valves 11 and 13 remain closed while valve 12 is opened to permit heated gases such as air, methane and other gases which have no deleterious effect on the zeolite to pass through the vessel being regenerated. The temperature of the regenerating gas should preferably be in the range of 15 400° to 550° F. If the gas being used for regeneration contains some moisture, it may be desirable to first pass the gases coming through a drier of known type containing activated alumina or silica gel before delivering 20 said gas to the adsorbent bed to be regenerated. During the regeneration operation the valves 6, 18 and 22 are closed while valve 15 is open. The gas exiting through the valve 15 contains essentially all the  $H_2S$  that had been adsorbed in the zeolite bed. This regenerating gas can be scrubbed with suitable solvents to remove a major portion of the  $H_2S$  contained therein or said regenerating gas can 25 be exhausted to the atmosphere. If the regeneration gas is heated methane or heated natural gas it can, after picking up the  $H_2S$  from the zeolitic adsorbent, be used as a fuel when the  $H_2S$  is destroyed by oxidation to  $SO_2$ .

30 Heating of the regenerating gas is commonly carried out in some external furnace. However, it is also within the purview of this invention to introduce a cool gas to the adsorbent vessels for regenerating and raise the temperature of the gas prior to regenerating by the means of 35 heating coils 31, 32 and 33, located in the bottom of the adsorbent vessels 1, 2 and 3, respectively. It is also contemplated that the beds within the adsorbent vessels need not be established as one continuous bed but could be contained therein as a series of superimposed beds with heating coils between the beds.

40 To prepare the beds for return to the adsorption cycle after regeneration, beds have to be cooled down to the adsorption temperatures of -40° to 150° F. For this step external sulfur-free cooling gases may be added through line 30 with valves 17 and 18 closed and valves 19 and 29 open. When an external sulfur-free cooling gas is employed to cool the 45 regenerated zeolitic adsorbent bed, the purified gas passes from the adsorption vessel into line 35 through the valve 36. At the same time the valves 38 and 37 are closed. Generally it is preferred that the cooling of the regenerated bed be accomplished by employing the cool gas derived from the adsorption operation carried out in one of the other vessels. During this 50 operation the valves 29, 36, 37 and 38 are closed while valves 17 and 19 are open. This permits the gas to flow from the vessel 1 to the vessel 3 for cooling operation. To recover the purified gas coming from the adsorption and cooling steps, said gas passes through valve 24 into the line 34 and thus delivered to storage or to process use. Since the purified gas leaving the vessel 3 during the initial stages of cooling has a temperature higher than that desired for storage or process, the gas may pass through a heat exchanger 25 to cool said gases to desired temperatures. During the initial cooling step a small amount of the purified carbon dioxide having picked up some impurities left during the previous regeneration step is purged from the system through line 27 by opening valve 28 during the purging interval. At the same time valve 26 is closed. After the impurities have been removed by purging during initial cooling the valve 28 is closed and the thus purified  $CO_2$  is removed from the system through the valve 26. When cooling takes place in the vessels 1 and 2 in the proper sequence, the purified gases are directed into line 34 through appropriate valves 20 and 22 and the gases are cooled by means of the corresponding heat exchangers 21 and 23.

55 It is to be understood that the process need not be performed in the apparatus shown in the drawing but may be performed in other suitable equipment without departing from the scope of the invention. Actually, the process could be carried out batchwise in one vessel but such procedure would not be practical on a large scale operation. One very effective variation of the arrangement of apparatus is the use of four separate adsorbent vessels; two connected in series for adsorption and one each for regeneration and cooling. In this manner, the first adsorption vessel can be operated at a much higher loading of  $H_2S$  and not be restricted by a limiting break-through of  $H_2S$  in amounts of 2 p.p.m. The carbon dioxide leaving the first adsorber with a  $H_2S$  content over 2 p.p.m. will continue to pass through the second adsorber where the excess  $H_2S$  is retained. When it has been determined that the first adsorber has been sufficiently loaded, the operation is switched to the second cycle. At this instant the first adsorber begins to be regenerated, the second adsorber begins to function as the initial adsorber and the vessel which was being cooled during the first cycle is connected therewith to function as the second adsorber. At the same time the vessel which was regenerated during the first cycle is now connected with a stream of sulfur-free cooling gas.

60 Generally, the pressure of the regenerating gas and the sulfur-free cooling gas should be

5 at or only slightly above atmospheric pressure to prevent disturbance of the adsorbent beds. However, in some cases no detrimental effects have become apparent by operating at pressures of up to 40 to 60 psig, when a sieve plate was placed above the beds of zeolitic adsorbent granules.

10 The chief factor which is instrumental in the production of the super-purified  $\text{CO}_2$  gas is the direction in which the regenerating and cooling gases flow through the zeolitic beds. It has been found that if the regenerating and sulfur-free cooling gases, particularly the sulfur-free cooling gases, pass through the 15 zeolitic beds in a direction countercurrent to the direction of the flow of gases during the adsorption cycle, such practice would eliminate the tendency for the adsorbed  $\text{H}_2\text{S}$  which is entrained in the zeolitic material even after regeneration to become redistributed throughout said material. It has been discovered that if the cooling operation is conducted in such a manner that the sulfur-free cooling gas passes 20 cocurrently through the zeolitic beds with respect to the absorption cycle, the subsequent 25 adsorption cycles become shorter. The reason for this phenomena regarding the cocurrent flow of cooling gases is that the sulfur compounds adsorbed in the inlet portions of the 30 zeolite material are moved down to the exit end of the vessel and thus decrease the next adsorption step by leakage of sulfur compounds therefrom. However, we have discovered that if cooling is done counter-currently then the 35 following adsorption cycles do not decrease with respect to the time at which the hydrogen sulfide reaches a breakthrough point of 2 p.p.m. This is illustrated in the Table set forth below.

#### EXAMPLE

40 In the practice of this invention, an artificial zeolite bed was established in a reactor similar to that illustrated as vessel 1 in the accompanying Figure, said zeolite contained therein having been dehydrated by heating to a temperature of  $350^\circ \text{ C}$ . until no further amounts of 45 water of crystallization were removed. This synthetic zeolite, having a chabazite crystalline structure, contained interstitial voids with the narrowest dimension measuring about 5 Angstrom units. The zeolite bed occupied 50 volume of about 100 c.c. and weighed about 65 grams. During the adsorption operations the temperature and pressure of the gases being purified were respectively  $100^\circ \text{ F}$ . and 350 psig. For regeneration the gas used was a dry  $\text{CO}_2$  which had been heated to  $500^\circ \text{ F}$ . and which was maintained at a pressure of about 10 psig. The cooling step was carried out by the use of a water-free and sulfur-free carbon dioxide which had a temperature of  $100^\circ \text{ F}$ . and a pressure of 10 psig.

55 The results of several runs set forth in the Table below clearly show the marked improvement in the process of purifying carbon dioxide by following the method of this invention. Runs 1—5 inclusive show a rapidly decreasing 60 adsorption cycle when cocurrent cooling is employed to prepare the zeolitic bed for further adsorption of the  $\text{H}_2\text{S}$  contained in  $\text{CO}_2$  gas. Immediate and continuous improvement 65 in the adsorption time is shown when the cooling operation is performed so that the cooling gas will pass through the zeolitic bed in a manner countercurrent to the flow of gases 70 during adsorption.

75

50

55

60

65

70

75

TABLE

Runs	H <sub>2</sub> S Content of Inlet Gas to Adsorption	Time of Absorption Cycle at breakthrough of 2 p.p.m. H <sub>2</sub> S	Remarks
1	415 p.p.m.	20.5 hrs.	Fresh adsorbent
2	395 "	29.0 "	Complete regeneration at 500° F.
3	400 "	12.0 "	3 hour regeneration with cocurrent cooling
4	370 "	6.5 "	After another 3 hour regeneration with cocurrent cooling
5	435 "	2.5 "	After another 3 hour regeneration with cocurrent cooling
6	360 "	5.75 "	Adsorbent from Run No. 5 subjected to 3 hour regeneration but with countercurrent cooling
7	350 "	8.5 "	Adsorbent from Run No. 6 subjected to 3 hour regeneration but with countercurrent cooling

## WHAT WE CLAIM IS:—

1. A method of separating gases containing carbon dioxide from at least one of the sulfur containing compounds hydrogen sulfide, carbon oxy sulfide or mercaptans which comprises passing the dried or undried gases containing CO<sub>2</sub> and at least one of said sulfur containing compounds through a zeolitic material to preferentially adsorb said sulfur containing compound or compounds, said zeolitic material having been previously activated by heating to drive off the water of crystallization to establish a crystalline structure having interstitial voids whose narrowest dimension is 4.0 Angstrom units or greater, continuing adsorption until the sulfur containing compound breakthrough reaches from 1 to 2 ppm, discontinuing adsorption, regenerating the adsorbent bed by passing a heated regenerating gas through the adsorbent in a manner countercurrent to the flow of gases during adsorption, preparing said adsorbent bed for further adsorption by passing a sulfur-free cooling gas through said bed, countercurrent to the direction of flow of gases during adsorption and recovering separately the purified carbon dioxide and the said sulfur containing compound or compounds.

2. The method according to claim 1 in which the pressure of the gases passing through the adsorbent bed is in the range of 200 to 500 psig.

3. The method according to claim 2 in which the regenerating gas is heated to 400 to 500° F. and the pressure of said regenerating gas is about atmospheric. 35

4. The method according to claim 3 in which the sulfur-free cooling gas reduces the temperature of the adsorbent bed to temperatures within the range of -40° F. to 150° F. 40

5. A method according to claim 4 in which the narrowest dimension of the interstitial void of the zeolitic adsorbent is about 5.0 Angstrom units. 45

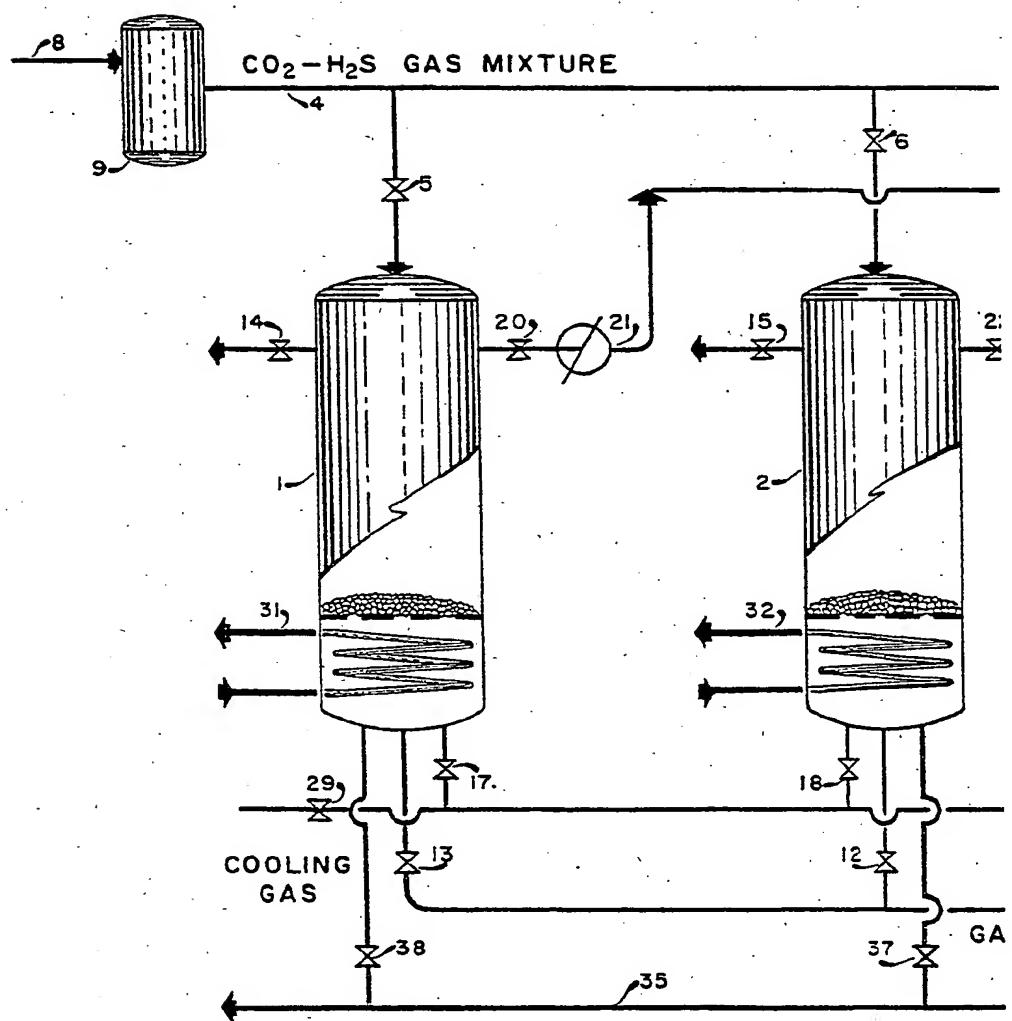
6. The method according to claim 1 in which the adsorption, regeneration and cooling operations are respectively performed simultaneously in three separate beds of adsorbent zeolite. 50

7. The method according to claim 1 in which the adsorption, regeneration and cooling operations are performed simultaneously in four separate beds of adsorbent zeolite whereby the gases pass sequentially through the first adsorption bed then through the second bed connected in series with the first bed while simultaneous regeneration and cooling operations are respectively performed in the third and fourth beds. 55

8. A method of separating gases containing carbon dioxide from at least one of the sulfur containing compounds hydrogen sulfide, carbon oxysulfide or mercaptans according to claim 1, substantially as hereinbefore described.

STEVENS, LANGNER, PARRY &  
ROLLINSON,  
Chartered Patent Agents,  
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1961.  
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which  
copies may be obtained.

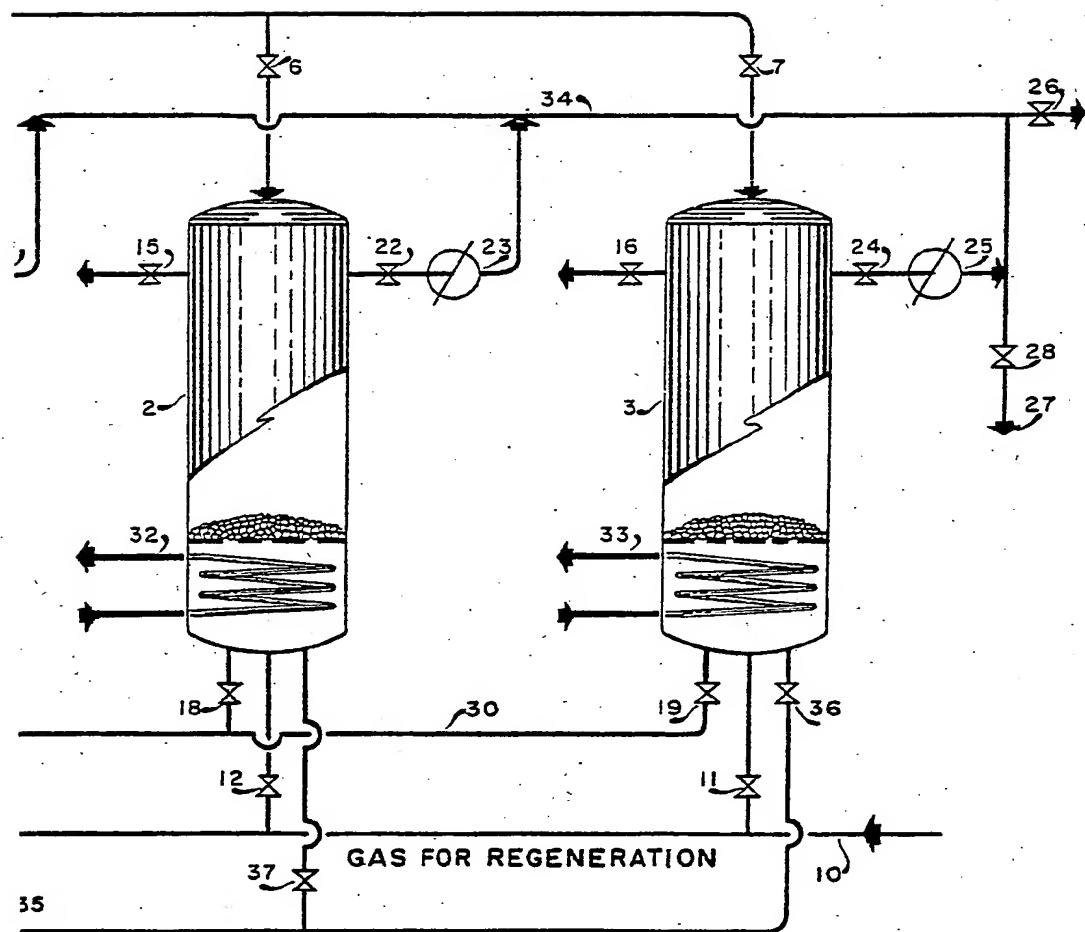


871750

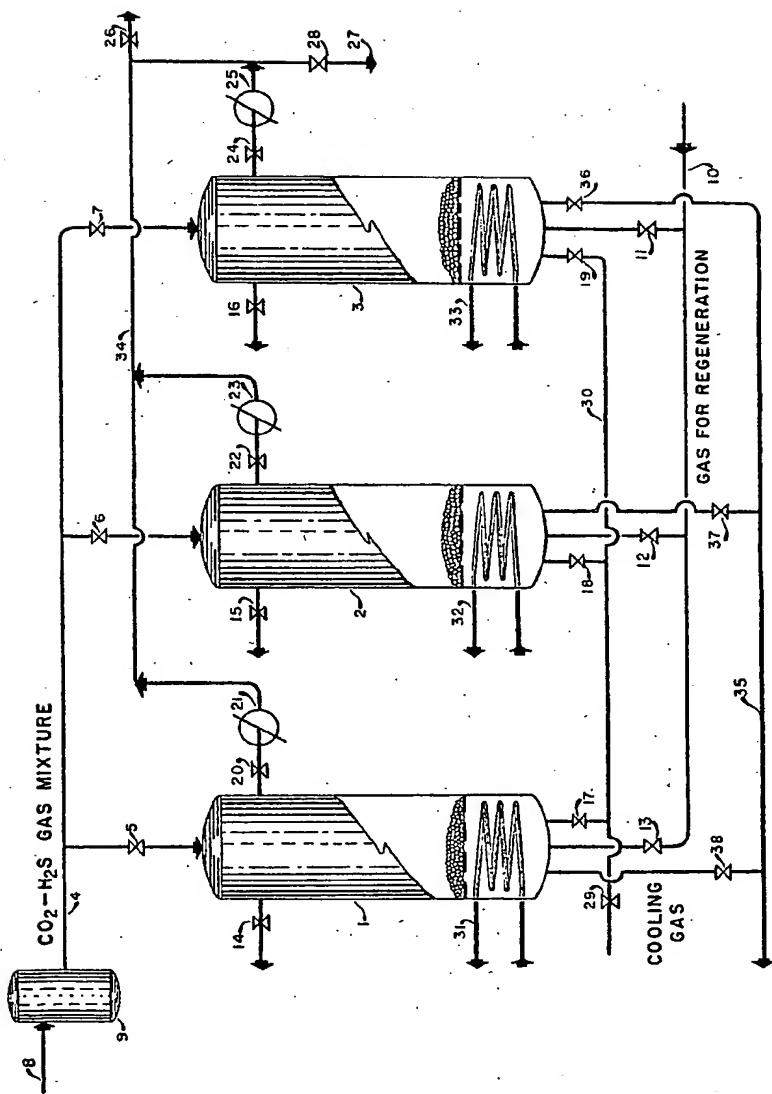
COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of  
the Original on a reduced scale*



871750 COMPLETE SPECIFICATION  
1 SHEET This drawing is a reproduction of  
the Original on a reduced scale



**THIS PAGE BLANK (USPTO)**